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Characterization of Aged Radioactive Pollucite

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Characterization of Aged Radioactive Pollucite

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CONTENTS

Summary 1

1 Introduction 2

2 Methods 4

3 Results 6

4 Proposed Future Work 12

5 Acknowledgments 13

6 References 14

FIGURES

1 Fluorescence from the ^{137}Cs-doped pollucite specimen taken with incident energy above the Ba K edge (blue) and below the Ba K edge but above the Cs K edge 7

2 XANES spectra from the Cs K edge of ^{137}Cs-doped pollucite and from nonradioactive pollucite 8

3 XANES spectra from Ba K edge of ^{137}Cs-doped pollucite, nonradioactive pollucite, and barium oxide 9

4 k-weighted EXAFS spectra from the Cs K edge of ^{137}Cs-doped pollucite and nonradioactive pollucite 10

5 k-weighted EXAFS spectra from Ba K edge of ^{137}Cs-doped pollucite, nonradioactive Ba-doped pollucite, and BaO 11

CHARACTERIZATION OF AGED RADIOACTIVE POLLUCITE

SUMMARY

The objective of this task was to provide information to better understand the long-term effects of decay on the stability of crystalline *pollucite* ($CsAlSi_2O_6$, also known as *Cs-leucite*). This decay is a key scientific issue in the assessment of the long-term stability, and hence performance, of pollucite as a waste form for ^{137}Cs. Most previous work on radiation effects in waste forms focused on alpha radiation, which produces more displacements per decay than beta radiation. However, the results of decay with beta radiation, which changes both the ionic radius and the valence of the element undergoing decay (0.160 nm for Ba^{2+} vs. 0.188 nm for Cs^{+}), are likely to predominate over cascade damage. The resulting changes in coordination chemistry may destabilize the waste form, permitting release of radionuclides to the accessible environment.

A small amount of Cs pollucite containing ^{137}Cs was embedded in epoxy "blocks." The isotopic composition of this material was $^{137}Ba_{0.0175}{}^{137}Cs_{0.02}{}^{133}Cs_{0.9625}AlSi_2O_6$ with the following ratios: ^{137}Cs/total Cs = 0.02, and ^{137}Ba/total Cs = 0.0175. A control sample of Ba-doped pollucite was also prepared.

We used x-ray absorption spectroscopy (XAS) to obtain barium and cesium spectra from a 10% Ba-doped nonradioactive pollucite sample and a ^{137}Cs-pollucite sample. The XAS analysis was done at the Materials Research Collaborative Access Team (MRCAT) beamline 10ID in Argonne's Advanced Photon Source (APS).

On the basis of x-ray fluorescence intensity, the radiogenic Ba fraction is 4±1% of the total cesium content of the sample. This result is in line with calculations based on the ^{137}Cs decay half-life and the original ^{137}Cs content of the sample. Therefore, the sample had much more than the minimum Ba content required for detection.

Detailed quantitative fitting of the spectra has been undertaken, but to date the results are incomplete. We compared the spectra of the Ba-doped pollucite to ^{137}Cs-leucite and also BaO in the case of the Ba K edge. At both of the absorption edges, the x-ray absorption near-edge structure (XANES) spectra are similar, but not identical between the radioactive and nonradioactive samples. In both cases, additional intensity is observed for the ^{137}Cs-containing sample. Furthermore, comparing the Ba spectra from radioactive pollucite to that obtained from BaO indicated that a distinct BaO phase is not segregating (exsolving) from the pollucite as Ba is generated. Although not conclusive, the correspondence of these changes suggests that the Ba remains incorporated in the Cs-leucite lattice, and the beta-decay energy has not entirely disrupted the crystal structure.

1 INTRODUCTION

The objective of this task (completed in 2008) was to provide information to better understand the long-term effects of decay on the stability of crystalline pollucite ($CsAlSi_2O_6$). This process is a key scientific issue in the assessment of the long-term stability, and hence performance, of pollucite as a waste form for ^{137}Cs. Most previous work on radiation effects in waste forms focused on alpha radiation, which produces more displacements per decay than beta radiation. However, the results of decay with beta radiation, which changes both the ionic radius and the valence of the element undergoing decay (0.160 nm for Ba^{2+} vs. 0.188 nm for Cs^{+}), are likely to predominate over cascade damage. The resulting changes in coordination chemistry may destabilize the waste form, permitting release of radionuclides to the accessible environment. Potential waste forms for Cs storage include silicate glass, glass-ceramics, cesium-loaded zeolites, and pollucite. Of these candidates, pollucite offers several advantages. It can accommodate more than 40 wt% Cs into its structure, thereby producing a highly dense waste form, comparable in density to glass and much denser than the glass-ceramic or zeolite alternatives. In addition, the measured and calculated dissolution rates of pollucite and the leachability of Cs in the pollucite structure are all about three orders of magnitude less than those measured for the candidate silicate glass [1]. The response of pollucite to radioactive decay, however, could adversely affect these advantages. Although the pollucite structure can accommodate > 40 wt% Cs, available data indicate that it can accommodate only about 10 wt% Ba [2].

Little is known about the mobility of Cs in pollucite. Only a few studies [3-5] have examined leaching following transmutation or irradiation of pollucite or closely related aluminosilicates, and the results seem to be inconsistent. The results may indicate that prior to radiation-induced amorphization, the accumulated defects can lead to higher leachability of Cs [3], whereas once amorphization occurs, the Cs becomes trapped in the collapsed structure [2]. A more thorough analysis of the effect of accumulated defects from both transmutation and ionization processes on the pollucite structure is needed to assess the impact on Cs mobility.

We selected pollucite for this study for the following reasons:

- We have access to as many as six well-characterized samples of ^{137}Cs-containing pollucite that had been stored under ambient conditions for 18 to 28 years. Most of these samples are contained in sealed stainless steel capsules, although one (the oldest, containing the most radiogenic barium) was opened for study as part of the DOE Office of Environmental Management Science Program (EMSP) in 1998 [6,7]. Small specimens were taken from this capsule for examination by electron microscopy and x-ray spectroscopy—these were the topic of this year's activities. The remaining capsules, and possibly the remaining material from the opened capsule, have been stored since 1999 in a shielded cask owing to their high radioactivity.

- Cesium-137 has a high activity ($t_{1/2}$ = 30.13 years), leading to the buildup of significant levels of Ba in these samples.

- Cesium continues to be an important constituent of the waste management effort within the DOE complex. A process for safe handling, storage, and disposal of ^{137}Cs is key to successful implementation of an advanced nuclear fuel cycle.

Pollucite, also known as Cs-leucite, has a cubic symmetry (space group *Ia3d*) at temperatures above ~100ºC. The crystal structure consists of a network of vertex-sharing (Si, Al)O_4 tetrahedra. The Cs is contained in wide channels that are parallel to the <111> directions. These channels do not intersect but are connected via <110> side channels. At temperatures below 100ºC, pollucite undergoes a reversible displacive phase transition to a tetragonal phase, which has spacegroup $I4_1/a$. Because the c/a ratio of the tetragonal phase is only 1.0051, it was not recognized as a distinct phase until recently [8].

If the structure of the pollucite is damaged by radioactive decay, it may be less effective at containing the ^{137}Cs. We focused this effort on determining whether the chemical differences between cesium and barium reduce the structural integrity of the pollucite and affect its crystal structure or the process of exsolving a second phase containing Ba. It was expected that the decay of ^{137}Cs to ^{137}Ba in the radioactive specimen would place the pollucite structure under significant strain, owing to the limited solubility of Ba in pollucite [2].

2 METHODS

A small amount of material (approximately microgram quantities) available for experimental investigation from the EMSP project came from an opened capsule bearing the serial number AD92, which was manufactured in 1979 [6,7]. From this material, there were 3 epoxy "blocks" available, which contain a small fragment of the material on an exposed face. The isotopic composition of this material, based upon information provided by the manufacturer, is given as:

Initial composition:

$$^{137}Cs_{0.0375}{}^{133}Cs_{0.9625}AlSi_2O_6$$

Composition as of 2007:

$$^{137}Ba_{0.0175}{}^{137}Cs_{0.02}{}^{133}Cs_{0.9625}AlSi_2O_6$$

$$^{137}Cs/\text{total Cs} = 0.02,\ ^{137}Ba/\text{total Cs} = 0.0175$$

We used x-ray absorption spectroscopy (XAS) to obtain the barium and cesium spectra from a 10% Ba-doped nonradioactive pollucite specimen. This is important because the overlapping of Cs-L edges with the Ba-L edges precludes normal fine structure analysis of the XAS (EXAFS) except from the relatively weak Ba-L_1 edge. Also, an effect known as "lifetime broadening," makes EXAFS from the K edges particularly weak. This work on nonradioactive pollucite was done at the Advanced Photon Source (APS) synchrotron, Argonne National Laboratory. The information gained was used to plan future EXAFS measurements on aged, radioactive pollucite specimens from the AD92 capsule at the APS.

X-ray absorption experiments were conducted at the MRCAT beamline 10ID at Argonne's APS. A cryogenically-cooled Si(111) monochromator selected the incident energy, and a Pt-coated mirror was used to reject the higher energy harmonic content in the beam. Due to the high energy absorption edges (Cs ~35985eV and Ba ~37440eV), the undulator insertion device was operated with the 7th harmonic. To observe the effects of energy resolution of the incident X-ray beam, we performed experiments with the Si(333) reflection, which has nominally 1/9 the bandwidth of the (111) reflection, but also about 2% the flux, due to mismatch to the source divergence and much greater demands on optical stability. The harmonic rejection mirror cutoff angle is critical in this configuration as the Si(444) reflection is also allowed. A factor of ~10 reduction in the Si(444) reflection intensity was achieved with the mirror set optimally.

For the ^{137}Cs-doped pollucite, the experiment was run by employing a microprobe, which permitted use of a smaller sample. The smaller sample resulted in less background radiation to the detector and an improved signal-to-noise ratio. Rhodium-coated mirrors in the Kirkpatrick-Baez geometry were used to focus the incident beam to less than 10 microns x 10 microns. The sample size was about 30 microns x 60 microns (file: *mar08/csba-grid.004*).

To detect the Cs and Ba fluorescence, 12 elements from a germanium solid-state detector were used with windows set on the Kα fluorescence lines. The energy resolution at 31 keV was about 500eV: sufficient to resolve the Cs and Ba Kα fluorescence lines at 30970eV and 32200eV, respectively, but insufficient to resolve the $K\alpha_1$ from the $K\alpha_2$ fluorescence (files: *mca_123.000 and mca_124.000*).

Data processing and analysis was performed with the *Athena* and *Artemis* software packages, based on *feffit* [9,10]. Model calculations of the EXAFS scattering paths were made using *feff* (version 8.28) [11].

3 RESULTS

On the basis of the X-ray fluorescence intensity (Figure 1), the radiogenic Ba fraction was 4%±1% of the total Cs content of the sample. This result is in line with the calculations based on the ^{137}Cs decay half-life and the original ^{137}Cs content of the sample. Therefore, the sample had much more than the minimum Ba content required for detection. Based on these data, the minimum measurable Ba content for spectroscopy is in the neighborhood of 0.2% of the Cs, albeit with extremely long data acquisition times.

Detailed quantitative fitting of the spectra has been undertaken, but to date the results are ambiguous for some of the same reasons given by previous researchers on these kinds of samples (i.e., core-hole lifetime broadening and artifacts at low radial distance). Nonetheless, important conclusions are possible from a qualitative analysis of the raw XAFS spectra.

Figures 2 and 3 show the Cs and Ba K edge spectra, respectively, of nonradioactive Ba-doped pollucite compared to ^{137}Cs-leucite and also BaO in the case of the Ba K edge. At both of the absorption edges, the XANES spectra are similar, but not identical between the radioactive and nonradioactive samples. In both cases, additional intensity is observed near the white line for the ^{137}Cs-containing sample. Furthermore, comparing the Ba pollucite spectra to BaO, it is apparent that a bulk BaO phase is not segregating from the pollucite as Ba is generated.

Figures 4 and 5 show the chi data with the background subtracted for the Cs and Ba K edge EXAFS, respectively. This presentation of the data also shows that the Ba spectrum changed in a similar way to the Cs spectrum. Although not conclusive, the correspondence of these changes suggests that the Ba remains incorporated in the Cs-leucite lattice, and the beta-decay energy has not entirely disrupted the crystal structure.

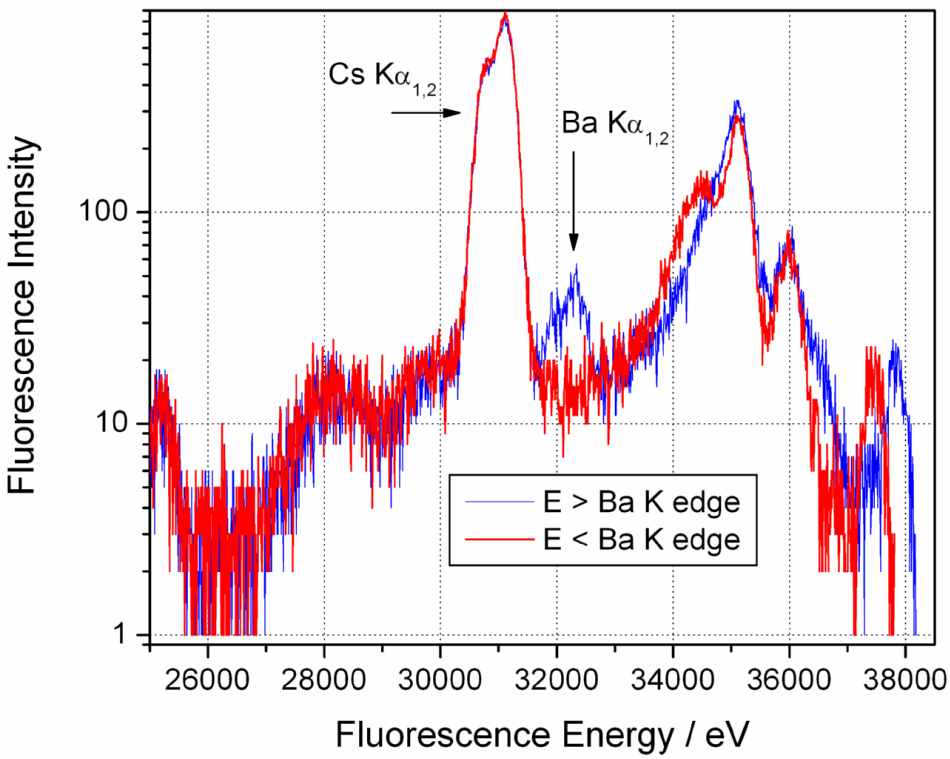

FIGURE 1 Fluorescence from the ^{137}Cs-doped pollucite specimen taken with incident energy above the Ba K edge (blue) and below the Ba K edge but above the Cs K edge (red). The weak Ba signal is consistent with the expected radiogenic fraction and the initial doping concentration of ^{137}Cs.

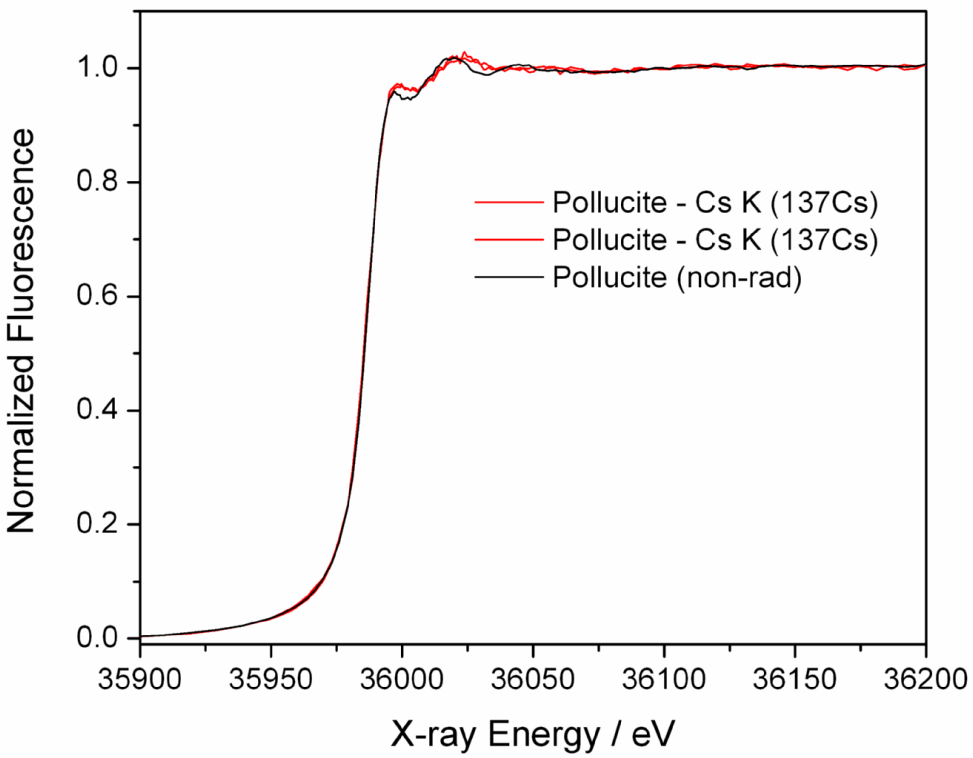

FIGURE 2 XANES spectra from the Cs K edge of ^{137}Cs-doped pollucite (red, two independent scans) and from nonradioactive pollucite (black).

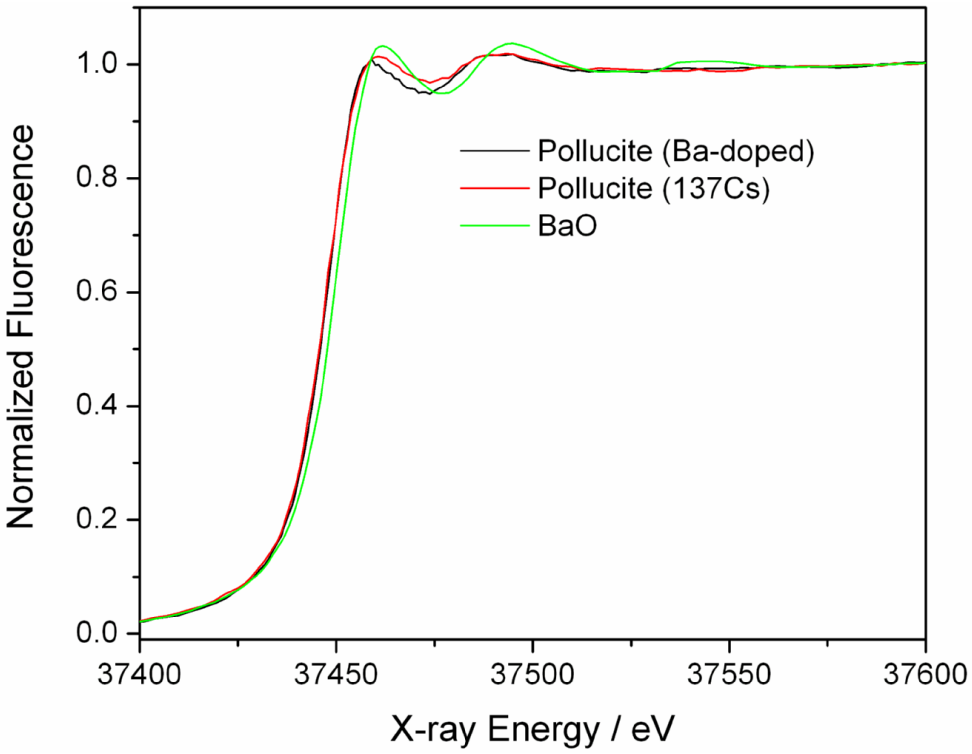

FIGURE 3 XANES spectra from Ba K edge of ^{137}Cs-doped pollucite (red), nonradioactive pollucite (black), and barium oxide (green).

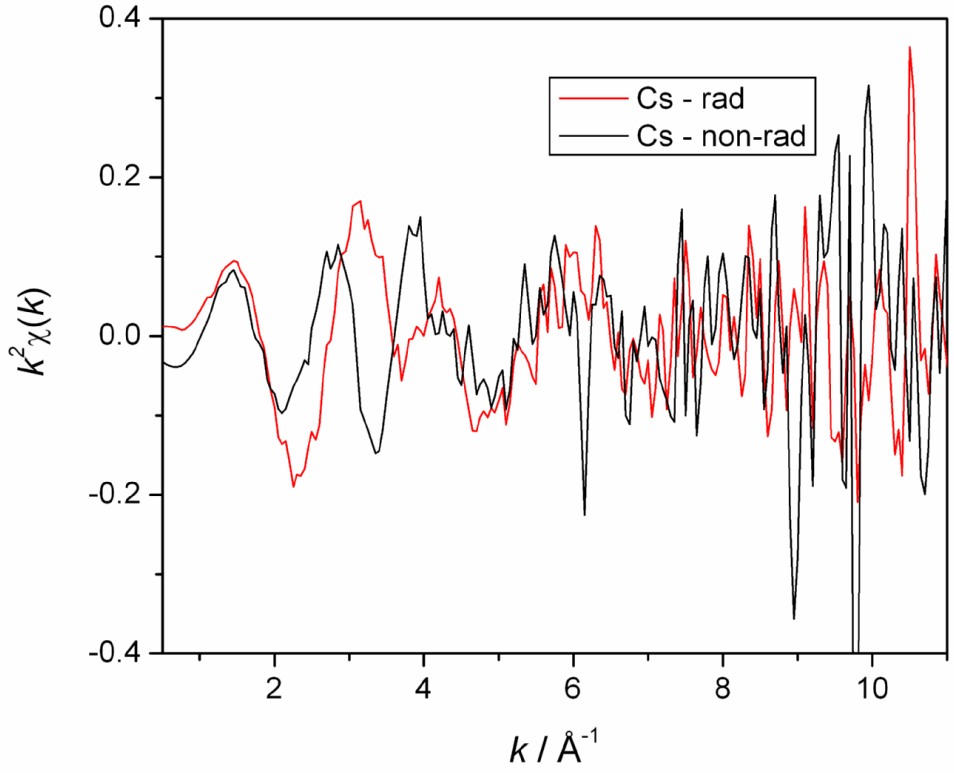

FIGURE 4 k-weighted EXAFS spectra from the Cs K edge of ^{137}Cs-doped pollucite (red) and nonradioactive pollucite (black).

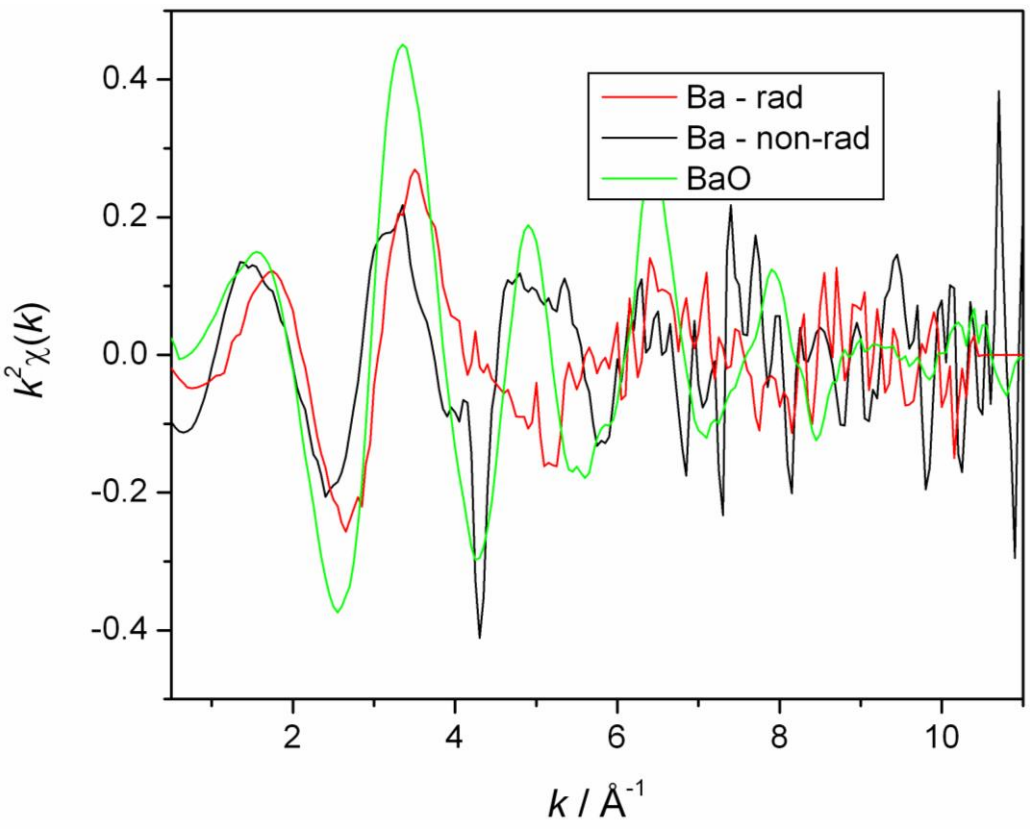

FIGURE 5 k-weighted EXAFS spectra from Ba K edge of ^{137}Cs-doped pollucite (red), nonradioactive Ba-doped pollucite (black), and BaO (green). The environment of the radiogenic Ba is clearly distinct from that in BaO or in the chemically doped pollucite.

4 PROPOSED FUTURE WORK

Further refinement of the XAS data may be possible, and additional data obtained from well-characterized materials such as *celsian* [$(Ba,Sr)Al_2(SiO_4)_2$] would likely be useful. Owing to the paucity of available ^{137}Cs-containing materials that have aged ~ 1 half-life or greater, it would be useful to simulate the effects of beta-decay using Argonne's low energy accelerator facility, which includes 3 MeV Van de Graaff and 20 MeV linac electron accelerators. This would allow the study of beta irradiation effects to be isolated from transmutation effects, and would provide greater opportunity to study the influence of temperature. It would also be useful to study the effects of annealing on the aged, radioactive material that provided the basis of this report, keeping in mind that the thermal study would be a destructive test on these rare specimens.

5

5 ACKNOWLEDGMENTS

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